Mat. Res. Soc. Symp. Proc. Vol. 722 © 2002 Materials Research Society

Growth of epitaxial ZnO films on Si(111)

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ABSTRACT

Epitaxial ZnO films have been grown on Si(111) substrates by employing a AlN buffer layer during a pulsed laser-deposition process. The epitaxial structure of AlN on Si(111) substrate provides a template for ZnO growth. The resultant films are evaluated by transmission electron microscopy, x-ray diffraction, and electrical measurements. The results of x-ray diffraction and electron microscopy on these films clearly show the epitaxial growth of ZnO films with an orientational relationship of ZnO[0001]||Aln[0001]||Si[111] along the growth direction and ZnO[2 $\bar{1}$ $\bar{1}$ 0]||AlN[2 $\bar{1}$ $\bar{1}$ 0]||Si[0 $\bar{1}$ 1] along the in-plane direction. High electrical conductivity (10^3 S/m at 300 K) and a linear I-V characteristics make these epitaxial films ideal for microelectronic, optoelectronic, and transparent conducting oxide applications.

INTRODUCTION

The need for blue and ultraviolet light emitting diodes and lasers has provoked enormous scientific and technological interest in II-VI and III-V wide band-gap semiconductors[1-5]. ZnO (bandgap of 3.27 eV at 300K) in II-VI semiconductor family[1,2] compares very favorably with GaN of III-V systems with almost identical bandgap and some additional advantages. To vary the bandgap of ZnO, it can be alloyed with MgO(8.2 eV) to increase the bandgap or with CdO(2.0 eV) to decrease it. This is similar to III-nitride system, where GaN is alloyed with AlN (6.2 eV) to increase the bandgap or with InN (1.8 eV) to decrease it. ZnO has a exciton binding energy of 60 meV compared to 25 meV for GaN, higher exciton binding energy results in less trapping of carriers and higher luminiscent efficiencies[2]. In addition to above, transition metal atoms(Mn, V, Fe, Co etc.) doped ZnO is a candidate of dilute magnetic semiconductors (DMS) that can be used as spintronic materials[4-7].

ZnO has a wurtzite structure with lattice constant of a=3.2498Å and c=5.2066Å. ZnO thin films have been grown by using several different techniques including pulsed laser deposition (PLD), plasma-assisted molecular beam epitaxy etc. It has been reported that ZnO thin films can be epitaxially grown on the (0001) oriented sapphire (α-Al_2O_3) substrate with a domain epitaxy growth mechanism (sapphire has a hexagonal structure of lattice constant of a=4.758Å and c=12.991Å). However, for the practical applications, the integration of ZnO thin films with Si substrate is more desirable. In this paper, we report the epitaxial growth of ZnO thin films on Si(111) substrate with AlN as a buffer layer by using pulsed laser deposition technique. AlN has hexagonal wurtzite structure with lattice constants of a=3.112 Å and c=4.982 A. The epitaxial growth of AlN thin films on Si(111) substrate occurs by the domain matching epitaxy[8], where integral multiples of major lattice planes of the film and the substrate match across the interface.

EXPERIMENT

The ZnO/AlN/Si(111) heterostructures were grown by pulsed-laser deposition using a KrF excimer laser (λ=248 nm, t_s=25 ns) in a high vacuum chamber. Before deposition, the silicon (111) substrate was cleaned to remove the surface oxide layer using 5% HF solution. The stoichiometric hot pressed AlN target obtained commercially was used to grow the AlN buffer layer. During the AlN buffer growth process, the Si (111) substrate was maintained at 750 °C, and the background pressure rose to 1×10^{-6} Torr. The AlN buffer layer was deposited at a laser energy density of 5J/cm^2 and pulse repetition rate of 10 Hz. ZnO target was made using standard ceramic method. ZnO powder was first calcined at 400 °C, then the resultant powder was pressed to round pellet of 2.54 cm diameter. The target was finally obtained by sintering the pellet at 1000 °C in following oxygen for 12 hours. ZnO thin films were deposited directly on the AlN buffer layer at 630 °C. The laser energy density and repetition rate were 2 J/cm^2 and 10 Hz, respectively. ZnO film was deposited first in vacuum (1×10^{-6} Torr) for 1 minute and then deposited at the partial oxygen pressure of 5×10^{-5} Torr. The total deposition times for AlN and ZnO thin films were 15 minutes each. The Crystal structures of these films were determined by using X-ray diffraction and transmission electron microscope. The conductivity of the film was also measured.

RESULTS AND DISSCUSION

The x-ray diffraction pattern of resultant thin film is given in Fig. 1. The diffraction pattern shows expected Si(111) family of planes together with AlN (002), AlN (004), ZnO (002), and ZnO(004) reflections. The XRD result shows that the ZnO and AlN films were crystalline with epitaxial characterizations on Si(111) substrate. The c axis lattice parameter of ZnO calculated from XRD data is found to be 5.199Å . The choice of AlN as a buffer layer was motivated by the earlier work of Narayan et al[8] in which they developed a metod to grow single crystal AlN films on Si(111) by domain matching epitaxy Here it is to be noted that there is a large difference between the lattice parameters of AlN and Si. The lattice misfit, f [defined as f=2(b-a)/(a+b), where a and b are the lattice parameters of the substrate and the AlN film, respectively] is 22.3%. This is a quite large value for lattice matching epitaxial growth. The epitaxial relationship between AlN film and Si(111) substrate was formed by the so called domain epitaxy mechanism (DEM), in which the dimensions of the domain become the repeat distance across which lattice matching is maintained. In each domain, 'm' lattice parameters (or interplanar distances) in the substrate match with 'n' in the epilayer, where, m and n are simple integers. The residual domain mismatch is given by f_d=2(nb-ma)/(nb+ma). In the case of AlN epitaxy on Si(111), 4 interplanar distances of Si(110) closely match with the 5 interplanar distances of AlN for AlN[$2\bar{1}\bar{1}0$]$\|$Si[$01\bar{1}$] epitaxial growth. This yields a domain misfit (f_d) of 1.2%, which is much smaller than the lattice misfit of 22.3%.

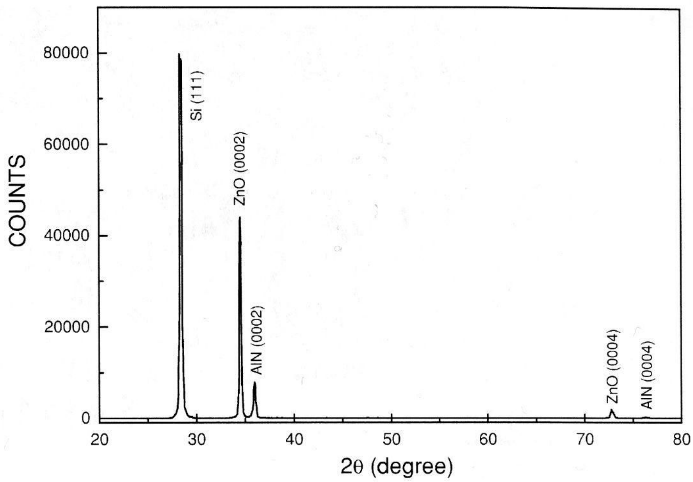


Fig. 1 X-ray diffraction pattern of ZnO film on AlN/Si(111).

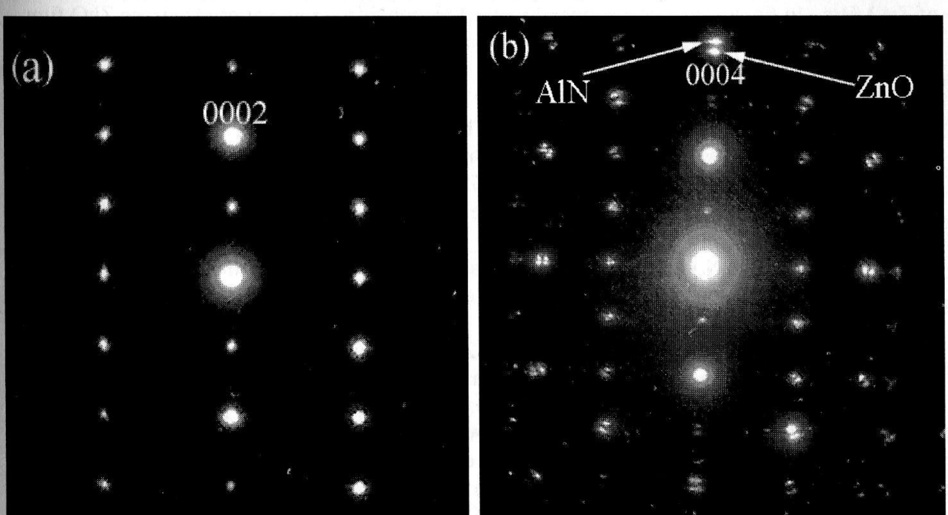


Fig. 2(a) selected area diffraction pattern from ZnO film; (b) selected area diffraction pattern from ZnO/AlN interface.

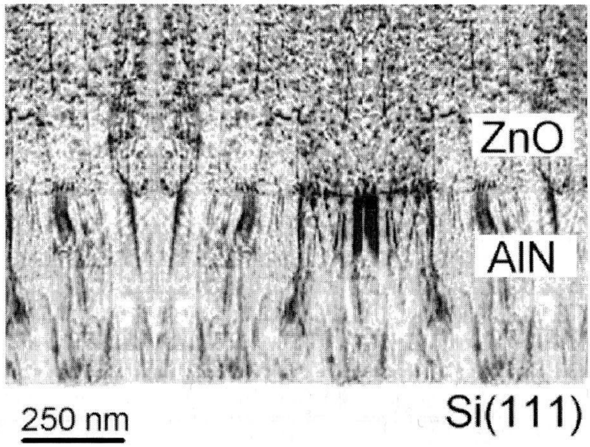
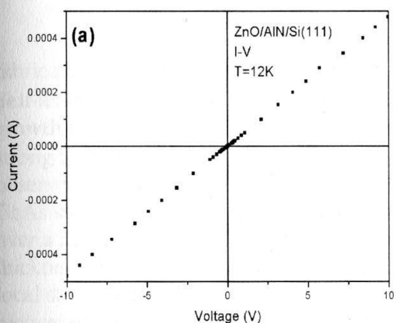


Fig.3 High resolution transmission electron photograph of ZnO/AlN/ Si(111).

Transmission electron diffraction studies confirmed the single crystalline epitaxial nature of ZnO film. In fig.2(a) we have shown the selected area diffraction pattern from the ZnO film, well aligned spots clearly establishes the high quality of the film. Figure 2(b) shows the selected area diffraction pattern taken from the ZnO/AlN interface. The orientational relationship between ZnO and AlN was ZnO[0001]||Aln[0001] along the growth direction and ZnO[$2\bar{1}\bar{1}0$]||AlN[$2\bar{1}\bar{1}0$] along the in-plane direction. The lattice misfit between ZnO and AlN is –4.3% by choosing AlN as substrate. This value is within the feasible range for lattice matched epitaxial growth. The negative sign means that ZnO is under compress stress corresponding to the tensile stress on the AlN buffer layer. Figure 3 shows the magnified cross sectional image along direction <$01\bar{1}0$> containing ZnO, AlN and silicon substrate. The micrograph clearly shows that the ZnO/AlN interface is atomically sharp. The film has a high concentration of stacking faults and dislocations, but still of very crystalline high quality.

Current versus voltage characteristics of ZnO films are shown in figure4. A linear relationship can clearly be seen. It again confirms the excellent quality of film and much less number of dislocations and stacking faults compared to films grown on sapphire. As mentioned earlier, the epitaxial feature for ZnO thin films on sapphire (0001) substrates occur by the domain matched epitaxy mechanism. There are edge dislocations on the boundaries of the domains. At least, one dislocation exists in each domain. As a result, there is a large density of dislocations on the ZnO/α-Al_2O_3 interface which gives nonlinearity in the I-V characteristics. Since the growth of ZnO films on AlN occurs by lattice matching, the density of dislocations is expected to be reduced significantly on the interface.

In summary, we have grown single crystal epitaxial ZnO films os Si(111) substrate by using AlN buffer layer. The sucessful growth of high quality ZnO films with silicon opens the opportunity for the integration of ZnO based optical and lasing devices with the next generation microelectronic devices.



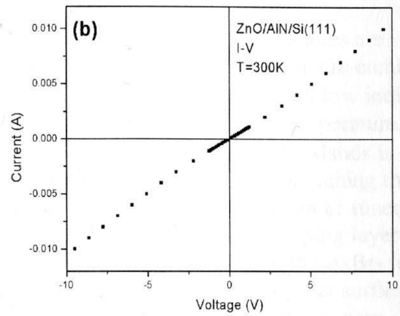


Fig.4 Current versus voltage (I-V) characteristics of ZnO film at 12K and 300K

ACKNOWLEDGMENTS

This research was supported by the US National Science Foundation Center for Advanced Materials and Smart Structure.

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